

Heats of formation for NF_n ($n = 1-3$) and NF_n^+ ($n = 1-3$)

Alessandra Ricca

Thermosciences Institute

NASA Ames Research Center

Mail Stop 230-3

Moffett Field, CA 94035

July 24, 1998

Abstract

Accurate heats of formation are computed for NF_n and NF_n^+ , for $n = 1-3$. The geometries and the vibrational frequencies are determined at the B3LYP level of theory. The energetics are determined at the CCSD(T) level of theory. Basis set limit values are obtained by extrapolation. In those cases where the CCSD(T) calculations become prohibitively large, the basis set extrapolation is performed at the MP2 level. The temperature dependence of the heat of formation, heat capacity, and entropy are computed for the temperature range 300 to 4000 K and fit to a polynomial.

1. Introduction

NF_n and NF_n^+ species are involved in etching and deposition reactions. Modeling of such processes requires accurate thermochemical information on the reacting species. Experimental heats of formation for the neutral species, NF_n ($n = 1-3$), are reported by JANAF [1]. The uncertainties associated with these values vary significantly with the number of fluorine atoms. For example the error bar for NF_2 is 1.9 kcal/mol while for NF the error bar is 7.9 kcal/mol. Theoretical heats of formation for NF_n were computed by Melius and Ho using the BAC-MP4 (SDTQ) approach [2]. Their values are smaller than the JANAF values for all systems, with a maximum difference of 5.6 kcal/mol for NF . The experimental heats of formation for the cations are obtained by using the heats of formation for the corresponding neutral species and their ionization potentials (IPs). The accuracy of the experimental IPs depends on the linear extrapolation of the yield curve to the zero limit. The determination of the ionization threshold can be affected by the presence of vibrationally excited molecules, molecules in metastable states or Rydberg states. In addition large geometry changes between the neutral and the ion can result in very small Franck-Condon factors making the determination of the adiabatic value very difficult. Given the uncertainty in the IPs and the heats of formation it is valuable to compute as accurately as possible the thermochemical values of both NF_n and NF_n^+ and compare them with experiment. In the present paper the coupled cluster singles and doubles approach [3], including the effect of connected triples determined using perturbation theory [4], CCSD(T), is used in conjunction with extrapolation to the complete basis set (CBS) limit to obtain accurate D_0 (298 K) values for systems as large as NF_2 and NF_2^+ . Unfortunately for NF_3 and NF_3^+ it is not possible to use this approach

due to large disk space requirements. An alternative way to obtain the CCSD(T) CBS values [5] is to correct the CCSD(T) results using the second-order Møller-Plesset [6] (MP2) CBS values and we use this approach for NF_3 and NF_3^+ .

2. Methods

Geometries are fully optimized and the harmonic frequencies computed using Density Functional Theory (DFT), in conjunction with the hybrid [7] B3LYP [8] functional and the 6-31+G* basis set [9]. The zero-point energy is computed as one half the sum of the B3LYP/6-31+G* harmonic frequencies. The DFT calculations are performed using Gaussian94 [10]. For open-shell molecules energetics are computed using the restricted coupled cluster singles and doubles approach [3,11] including the effect of connected triples determined using perturbation theory [4,12], RCCSD(T). In most calculations, only the valence electrons are correlated, namely the N 2s and 2p and F 2s and 2p. These calculations are performed using the augmented-correlation-consistent polarized valence (aug-cc-pV) sets developed by Dunning and coworkers [13-15]. We use the augmented triple zeta (ATZ), quadruple zeta (AQZ) and quintuple zeta (A5Z) sets. The CCSD(T) results are extrapolated to the basis set limit using several extrapolation techniques: the two-point scheme (n^{-3}) described by Helgaker et al. [16], the two-point (n^{-4}), three-point ($n^{-4} + n^{-6}$) and variable α ($n^{-\alpha}$) schemes described by Martin [17]. Core-valence (CV) calculations are performed by adding the N 1s and F 1s electrons to the correlation treatment. Three core-valence basis sets are developed and are denoted CV(tz), CV(qz) and CV(5z). They are derived from the corresponding aug-cc-pV sets by contracting the first five (CV(tz)), six (CV(qz)) and seven (CV(5z)) s primitives to one function for both

N and F. For all three basis sets, the rest of the s functions and all of the p functions are uncontracted. Three even-tempered tight d and two even-tempered tight f functions are added to both N and F in all three basis sets. A β value of 2.5 is used for the d functions and a value of 3.0 is used for f functions. The CV effect is computed as the difference between correlating only valence electrons and correlating the valence plus inner-shell electrons, with both calculations performed using the CV basis sets. All the CCSD(T) calculations are performed using Molpro96 [18].

In our recent study [19] on NF and NF⁺, we computed the spin-orbit effect for NF⁺ using a state-averaged complete-active-space self-consistent-field/internally contracted multireference configuration interaction (SA-CASSCF/ICMRCI) [20] calculation using Molpro 97.5 [21]. The spin-orbit effect was taken as one half the separation between the ²Π_{1/2} and the ²Π_{3/2} levels [22]. For all the remaining systems considered in the present work, the spin-orbit effect is obtained by using the accurately known spin-orbit splittings in the atoms. For the atoms, the difference between the lowest m_j component and the m_j weighted average energy [23] is used.

3. Results and Discussion

The computed and extrapolated bond energies reported in Table 1 are obtained by using geometries optimized at the B3LYP level of theory. To test the effect of geometry on bond energies we optimize both NF and NF⁺ using the ATZ, AQZ and A5Z basis sets at the CCSD(T) level of theory and we compute the bond energies by extrapolation to the basis set limit. The zero-point energies are computed using the corresponding CCSD(T) frequencies. For NF the bond energy changes by only 0.01 kcal/mol and for NF⁺ by only

0.16 kcal/mol. The error for the larger system NF_3^+ could be as large as 0.48 kcal/mol but most probably less. Therefore we can conclude that geometry does not affect the computed bond energies for the neutrals and affects only marginally the computed bond energies for the cations.

The three-point Martin ($n^{-4} + n^{-6}$) and the variable α extrapolated values are in very good mutual agreement for both CCSD(T) and MP2 results. The CBS values reported in Table 1 are the average of the three-point Martin ($n^{-4} + n^{-6}$) and variable α extrapolated values. The α values are usually between 4.0 and 4.7, confirming that the extrapolations are fairly accurate. For NF_3^+ the MP2 α value is 8.9 indicating some problems in the extrapolation. A comparison of the AQZ and A5Z MP2 values for NF_3^+ shows that they are almost identical which makes the extrapolation more difficult. Despite this difficulty we are confident that the NF_3^+ extrapolated value is accurate as the three-point Martin ($n^{-4} + n^{-6}$) and variable α extrapolated values are in reasonable agreement.

The MP2 bond energies are overestimated but the MP2/CCSD(T) ratio is virtually independent of basis set and can be used to obtain CBS CCSD(T) values [5]. In the case of NF_3 and NF_3^+ the CCSD(T) AQZ and A5Z calculations were intractable due to large disk space requirements and the CBS CCSD(T) values given in parentheses are obtained by multiplying the CCSD(T) (ATZ) values by the ratios MP2(CBS)/MP2(ATZ).

In our recent study [19] we computed the bond energies for NF and NF^+ with and without correcting for BSSE and extrapolated the values to the CBS limit. The BSSE effect does not affect significantly the extrapolated values and we do not evaluate it for the larger systems. The D_e CBS values for NF and NF^+ reported in Table 2 are obtained by taking

the average of the three-point Martin ($n^{-4} + n^{-6}$) and variable α values, computed with and without BSSE correction.

The D_e CBS values are corrected for CV effects, spin-orbit effects, zero-point energy, and thermal effects, and are reported in Table 2. The CV contribution for the neutrals is negligible (0.02 kcal/mol) and appears to be the same for all the neutrals. For the cations the CV contribution is slightly larger (0.27 kcal/mol) and also appears to be the same for all the ions. The bond energies are larger for the cations than for the neutrals. The difference is particularly important for NF and NF^+ . The N-F bond is stronger for the ground ($^2\Pi$) state of NF^+ than for the ground ($^3\Sigma^-$) state of NF due to some donation of the F π orbital to the empty N 2p orbital giving the cation some double bond character.

The bond energies at 298 K (D_{298}) are combined with the well-known experimental enthalpy of formation (at 298 K) of NF_3 [1] (-31.57 ± 0.27 kcal/mol) and of F [1] (18.97 ± 0.07 kcal/mol) to compute the enthalpies of formation given in Table 3. The enthalpy of formation of N^+ is obtained using the computed enthalpy of formation of N and the experimental IP of N [24] (335.165 ± 0.001 kcal/mol). Our enthalpy of formation of N is in very good agreement with the JANAF value. Given the excellent agreement for the atomization energy of NF_3 , we estimate that our maximum error bar is 2 kcal/mol. For the neutrals, our values lie between those of Melius and Ho and those of JANAF and they agree to within their error bars. For the ions, there is good agreement between our values and the experimental values of Lias [25] for NF^+ and NF_2^+ , while for NF_3^+ our value differs by 5 kcal/mol with experiment. This difference is surprising considering our estimated uncertainty. The value reported by Lias is obtained using the NF_3 heat of formation and its IP. Given the accuracy of our NF_3 atomization energy we suspect that

the difference is due to the experimental IP for NF_3 [26]. To test this hypothesis we compute the adiabatic ionization potentials for the NF_n^+ species using the CCSD(T) approach in conjunction with the ATZ, AQZ, and A5Z basis sets and the values are reported in Table 4 along with experiment [26,27]. We first note the weak dependence of the IP on the basis set for NF and NF_2 . Our best values are about 0.03 eV smaller than experiment, and even the ATZ values are only 0.06 eV too small. For NF_3 our value is 0.36 eV smaller than experiment. The computed adiabatic and vertical IPs for NF_3 differ significantly from each other due to large changes in geometry. An inspection of the experimental yield curve in reference [26] suggests that it is indeed difficult to extrapolate to the adiabatic limit. Our calculations suggest that the experimental adiabatic IP for NF_3 is too large by 0.2-0.3 eV.

We use our computed heats of formation at 298 K and the B3LYP geometries and frequencies to evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits can be found on the web [28].

4. Conclusions

Bond energies are obtained for NF_n and NF_n^+ , for $n = 1-3$, using the CCSD(T) approach and by extrapolation to the complete basis set limit. High accuracy is achieved by taking into account core-valence correlation effects, spin-orbit effects, zero-point energy, and thermal effects. The resulting bond energies at 298 K are used in conjunction with the accurately known heats of formation of NF_3 and F, and the IP of N to obtain the heats of formation of all the remaining systems. Our heats of formation agree with the experimental values and with the values of Melius and Ho within their respective error

bars. For NF_3^+ our computed value does not agree well with experiment. We suggest that the discrepancy is due to an overestimated experimental IP for NF_3 . The temperature dependence of the heat of formation, the heat capacity, and entropy are computed and fit to the standard 14 coefficients, which are available on the web.

Acknowledgments

A. R. would like to acknowledge helpful discussions with Charlie Bauschlicher. A.R. was supported by NASA Contract No. NAS2-14031 to ELORET.

References

- [1] M. W. Chase Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data* 11 Suppl. 1 (1985).
- [2] C. F. Melius and P. Ho, *J. Phys. Chem.* 95 (1991) 1410.
- [3] R. J. Bartlett, *Annu. Rev. Phys. Chem.* 32 (1981) 359.
- [4] K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* 157 (1989) 479.
- [5] A. Ricca and C. W. Bauschlicher, *J. Phys. Chem.* 102 (1998) 876.
- [6] J. A. Pople, J. S. Binkley and R. Seeger, *Int. J. Quantum Chem. Symp.* 10 (1976) 1.
- [7] A. D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [8] P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.

- [9] M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.* 80 (1984) 3265 and references therein.
- [10] Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
- [11] P. J. Knowles, C. Hampel and H.-J. Werner, *J. Chem. Phys.* 99 (1993) 5219.
- [12] J. D. Watts, J. Gauss and R. J. Bartlett, *J. Chem. Phys.* 98 (1993) 8718.
- [13] T. H. Dunning, *J. Chem. Phys.* 90 (1989) 1007.
- [14] R. A. Kendall, T. H. Dunning and R. J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [15] D. E. Woon, K. A. Peterson and T. H. Dunning, unpublished.
- [16] T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.* 106 (1997) 9639.
- [17] J. M. L. Martin, *Chem. Phys. Lett.* 259 (1996) 669.
- [18] Molpro96 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone and P. R. Taylor.
- [19] A. Ricca, *Chem. Phys. Lett.*, submitted.
- [20] H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* 89 (1988) 5803.
- [21] Molpro97 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, A. Berning, D. L. Cooper, M. J. O. Deegan,

- A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schutz, H. Stoll and T. Thorsteinson.
- [22] H. Lefebvre-Brion and R. W. Field, *Perturbations in the spectra of diatomic molecules* (Academic Press, Orlando, 1986).
- [23] C. E. Moore, Atomic energy levels, Natl. Bur. Stand. (US) circ. 467, 1949.
- [24] K. B. S. Eriksson and J. E. Pettersson, *Phys. Scr.* 3 (1971) 211.
- [25] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* 17, Suppl. 1 (1988).
- [26] J. Berkowitz and J. P. Greene, *J. Chem. Phys.* 81 (1984) 3383.
- [27] J. Berkowitz, J. P. Greene, J. Foropoulos Jr. and O. M. Neskovic, *J. Chem. Phys.* 81 (1984) 6166.
- [28] The values can be found at <http://www.ipt.arc.nasa.gov>

Table 1: Computed bond energies, in kcal/mol, without zero-point energies.

Molecule	Method	ATZ	AQZ	A5Z	CBS ^a	α^b
N-F	CCSD(T)	72.96	75.34	76.02	76.50	4.508
	MP2	76.27	78.56	79.31	79.94	3.914
NF-F	CCSD(T)	65.34	67.06	67.51	67.79	4.859
	MP2	70.64	72.44	73.0	73.45	4.083
NF ₂ -F	CCSD(T)	59.19			(60.96)	
	MP2	66.03	67.31	67.70	68.0	4.235
N ⁺ -F	CCSD(T)	125.89	128.50	129.21	129.69	4.675
	MP2	131.34	134.05	134.86	135.47	4.271
NF ⁺ -F	CCSD(T)	80.31	81.97	82.37	82.60	5.225
	MP2	86.91	88.69	89.20	89.56	4.514
NF ₂ ⁺ -F	CCSD(T)	34.52			(35.39)	
	MP2	39.11	40.02	40.11	40.09	8.875

^a Average of the three-point Martin ($n^4 + n^6$) and variable α extrapolated values. The values in parentheses are estimated using the CBS MP2 values.

^b The α value is obtained by the variable α extrapolation.

Table 2: Computed bond energies, in kcal/mol, corrected for core-valence effects, spin-orbit effects, zero-point energy, and thermal effects.

	D _e CBS	+CV	+SO	+ZPE	D ₂₉₈
N-F	76.62 ^a	76.64	76.25	74.62	75.57
NF-F	67.79	67.81	67.42	65.37	66.48
NF ₂ -F	60.96	60.98	60.59	57.97	59.21
N ⁺ -F	129.80 ^a	130.07	129.64	127.38	128.56
NF ⁺ -F	82.60	82.87	82.48	80.09	81.27
NF ₂ ⁺ -F	35.39	35.66	35.27	32.61	33.85

^a Average of the three-point Martin ($n^{-4} + n^{-6}$) and variable α extrapolated values, computed with and without BSSE correction.

Table 3: Enthalpies of formation, in kcal/mol, at 298° K.

	Present work	Melius & Ho [2]	JANAF [1]	Lias [25]
NF ₃	$(-31.57 \pm 0.27)^a$	-28.0 ± 1.4	-31.57 ± 0.27	
NF ₂	8.67	7.9 ± 2.2	10.1 ± 1.9	
NF	56.18	53.9 ± 1.9	59.50 ± 7.9	
N	112.78		112.97 ± 0.024	
N ⁺	449.65 ^b		449.84 ± 0.10	
NF ⁺	340.06			339.2 ^c
NF ₂ ⁺	277.76			275
NF ₃ ⁺	262.88			268

^a The value in parenthesis is taken from JANAF [1] and is used as a reference point.

^b The enthalpy of formation of N⁺ is computed from the enthalpy of formation of N, and the experimental IP(N), and the enthalpy of the electron.

^c The reported 0° K value is converted to 298° K.

Table 4: Computed adiabatic ionization potentials, in eV^{a,b}.

Molecule	Method	Present work			Experiment
		ATZ	AQZ	A5Z	
NF	CCSD(T)	12.20	12.22	12.23	Berkowitz [26,27] 12.26 ± 0.01
NF ₂	CCSD(T)	11.57	11.58	11.60	11.628 ± 0.01
NF ₃	CCSD(T)	12.64 (13.87)			13.00 ± 0.02

^a The value in parenthesis is the vertical ionization potential.

^b The values reported include zero-point energy.